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## (54) CONTROL OF EMULSION POLYMERISATION PROCESS

(71) We, POLYSAR LIMITED, a Company organised under the laws of Canada, of Sarnia, Ontario, Canada, do hereby declare the invention, for which we pray that a patent may be granted to us and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to an improved process for the control of a polymerization system, especially a free radical catalyzed polymerization of, for example, butadiene and styrene monomers in an aqueous emulsion, to yield a product of predefined quality.

Many polymerization processes are influenced by the presence of and the concentration of minor amounts of impurities which may enter the process by a variety of means. In a number of such cases the disturbance created in the polymerization process causes an upset in the quality of the product of the polymerization process. If the polymerization process has a long hold-up time, monitoring of the quality of the final product may lead to the production of considerable quantities of product of non-desired quality. Such processes may be exemplified by the free radical catalyzed polymerization of butadiene and styrene monomers in an aqueous emulsion to produce styrenebutadiene copolymers, the overall polymerization time in such a process being from about six hours up to about 18 hours. A disturbance in such a process could lead to the production of a considerable quantity of polymer before it was recognized that the disturbance had occurred and was causing the production of polymer which was not of the desired quality. In the early commercial operation of this process, control of the final product quality was largely achieved by monitoring by time consuming laboratory methods both the per cent conversion of monomers to polymer and the molecular weight of the polymer and by blending of polymers. Such control methods are not adequate for the production of polymer to meet the quality requirements of today. A prior art refinement of the control means was directed to a process wherein the flow rates and component concentrations, including impurities which could cause upsets in the process, were determined and used to manipulate the control of the catalyst and activator streams in order to achieve the desired monomer-to-polymer conversion. This prior art process required extensive use of analytical tools for the determination of the component concentrations.

It is an objective of this invention to provide a process for the production of a polymer using a novel manner of control whereby there is produced a uniform quality product, said novel manner comprising maintaining essentially constant the monomer conversion and the product molecular weight, both at predetermined desired values, through the aid of a computed mathematical simulation of the process thereby causing corrective control action to be taken in a shorter time than the actual residence time for the series of reactors, the polymerization process being exemplified by, but not limited to, an aqueous emulsion free radical catalyzed polymerization of butadiene and styrene.

In the process of this invention, the monomer-to-polymer conversion is measured, the polymer Mooney is determined on a periodic basis, a vistex viscosity of the polymer is measured and, together with the conventional process control measure-

ments such as flow rates of feed streams, these data are utilized in a special computational program so that the process may be controlled in a dynamic manner. The computer program is directed to the use of a mechanistic model based on the kinetics of the reactions involved and the theory of Harkins-Smith-Ewart adapted to a continuous polymerization process. Because the process of this invention has an unusually long residence time—i.e. from about 6 to about 12 hours—spread over a series of reactors the computational model must incorporate many of the previous control actions which could still be affecting the process. Thus a mathematical model is used to calculate the condition in each individual reactor of the chain, allowing for the interaction from one reactor to another of the results of prior control actions. The model may make use of measurement of monomer-to-polymer conversion at a point at least one third of the way down the series of reactors so that the response of the system to changes in the levels of impurities in the components fed to the system will be readily picked up and the system corrected to compensate for such changes.

The process comprises feeding at controlled flow rates a plurality of fluid feed streams to a plurality of reactors in series, each of said fluid feed streams being a major source of one of at least one polymerizable monomer, water, soap solution, catalyst, activator, modifier and polymerization stopping agent, said feeding of fluid feed streams being to at least the first reactor of a plurality of reactors in series each reactor being equipped with stirring means and temperature regulating means, and recovering a polymer of predetermined qualities. The polymer is recovered in suitable form, including as a solid dry rubber and as a latex containing a high level of polymer solids. Incorporated into the process layout are means for determining the conversion of the polymerizable monomers to polymer and means for determining a molecular weight of the polymer. Signals are generated responsive to the measurements made, as hereinbelow defined, and are transmitted on a periodic basis to a computing means.

Figure 1 is a schematic drawing of a feed control system for a free radical catalyzed emulsion polymerization process.

Figure 2 is a schematic drawing of a polymerization means for a free radical catalyzed emulsion polymerization process.

Figure 3 is a diagrammatic layout of an automated vistex viscometer which may be used, within the scope of a polymerization process, to determine a molecular weight of the polymer produced in the process.

Referring to Figure 1, storage is provided in drum 11 for butadiene-1,3, in drum 12 for styrene, in drum 13 for modifier, in drum 14 for water, in drum 15 for emulsifier solution, in drum 16 for activator, in drum 17 for catalyst and in drum 18 for increment modifier. Butadiene-1,3 is withdrawn from drum 11 through line 21, passing through flow measuring device 31 to flow control valve 41 and into line 61. Flow recorder controller 51 is preset to the required flow rate, a signal responsive to the required flow rate being transmitted to flow control valve 41; a signal responsive to the actual flow measured by flow measuring device 31 is transmitted to flow recorder controller 51 which, in response to the received signal, transmits a signal resetting, if necessary, flow control valve 41 in order to achieve the desired flow rate. A signal responsive to the flow rate is transmitted by flow recorder controller 51 to computing means 501. Similarly, styrene is transferred at a measured pre-established flow rate from drum 12 through line 22, flow measuring device 32 and flow control valve 42 to line 61, where it is blended with butadiene. Modifier from drum 13 is fed through line 23 to metering pump 33 which controls the rate of flow into mixed feed line 61. Water from drum 14 is passed via line 24 through flow measuring device 34 to flow control valve 44, said valve being set responsive to signals from flow recorder controller 54, and into line 62. Soap solution is transferred from drum 15 through line 25 to flow measuring device 35 to flow control valve 45, which is set in response to signals from flow recorder controller 55, into line 62 where it is admixed with the water. Activator from drum 16 is drawn through line 26 through flow measuring device 36 and flow control valve 46, said flow control valve being set responsive to signals from flow recorder controller 56, and into line 66. Catalyst from drum 17 is transferred through line 27 to metering pump 37 wherein the rate of flow is controlled into line 67. Increment modifier is withdrawn from drum 18 through line 28 to metering pump 38 wherein the rate of flow is controlled into line 68.

The butadiene-styrene-modifier mixture in line 61 is admixed with the water-soap solution of line 62, the mixture being transferred by line 63 to heat exchanger 71 wherein the whole stream is cooled to a predetermined temperature. The temperature of the cooled feed stream exiting from heat exchanger 71 is measured by

temperature measuring device 72; a signal responsive to said temperature is transmitted to temperature recorder controller 74 wherein it is compared with a pre-established set point and if the temperature measured is different from the set point a signal is transmitted from the temperature recorder controller to the flow control valve 73 whereby the flow of refrigerant supplied to heat exchanger 71 is controlled in order to achieve the pre-established temperature. Activator from line 66 and catalyst from line 67 are then mixed with the cooled feed stream in line 79 and the whole is passed into the first reactor 101.

Signals are generated responsive to the flow rates as recorded in flow recorder controllers 51, 52, 54, 55 and 56 and signals are generated responsive to the flow rates set by metering pumps 33, 37 and 38. A signal is generated responsive to the temperature recorded by temperature recorder controller 74. These signals are transmitted on a periodic basis to computing means 501. Similarly, computing means 501 may transmit signals for the establishment of new set points in said flow recorder controllers, metering pumps and temperature recorder controller.

Figure 2 represents a schematic layout of a polymerization means for this process. The cooled feed stream in line 79 is fed into reactor 101. Reactor 101 is equipped with an agitator 102, cooling means 104, temperature measuring means 106 and a temperature recorder controller 108. A signal responsive to the temperature determined by measuring means 106 is transmitted to temperature recorder controller 108 wherein it is compared with a pre-established set point. If the temperature determined is different from the set point, temperature recorder controller 108 transmits a signal causing the setting of flow control valve 109 to be altered thereby causing the flow of refrigerant to cooling means 104 to be altered so as to achieve the set point temperature. The effluent from reactor 101, which contains unreacted components of the original feed stream plus polymer formed during the residence in the reactor, passes through line 110 into the second reactor 111. Each reactor in the chain is essentially similar to each other reactor. The chain shown in Figure 2 comprises in addition to reactor 101, reactors 111, 121, 131, 151, 161, 171 and 181 each reactor being equipped with an agitator 112, 122, 132, 152, 162, 172 and 182, with a temperature measuring means 116, 126, 136, 156, 166, 176 and 186, and being equipped with cooling means 114, 124, 134, 154, 164, 174 and 184. Signals responsive to the temperatures as determined by the temperature measuring means are transmitted to temperature recorder controllers, respectively 118, 128, 138, 158, 168, 178 and 188, which regulate the flow of refrigerant through flow control valves 119, 129, 139, 159, 169, 179 and 189. The effluent from each reactor is transferred to the subsequent reactor in the chain by lines 120, 130, 160, 170 and 180: the effluent from reactor 131 is passed through line 140 to conversion measuring means 142 and by line 144 to reactor 151. Line 146 is a means for removal of samples for other purposes including solids determination and measurement of the molecular weight of the polymer in line 144. Although eight reactors have been shown to compose the chain, this is for illustrative purposes only and is not to be construed as a limitation on the invention.

The effluent from reactor 181 passes via line 190 to a conversion measuring means 192 and by line 194 to blow down tank 201. Line 196 is for removal of samples. Blow down tank 201 is equipped with an agitator 202, a vent line 204, an inlet line 206 for steam and a line 210 whereby the effluent is passed to finishing and recovery processes.

Shortstop is stored in drum 220 and is passed through line 222 through flow measuring device 224 to flow control valve 226 and thence by line 230 to blow down tank 201. The flow rate of shortstop, as measured by flow measuring device 224, is transformed to a responsive signal and transmitted to flow recorder controller 228 wherein it is compared with the pre-established set point and if a difference exists, flow recorder controller 228 transmits a signal to flow control valve 226 whereby the setting of said flow control valve is changed in order to restore the flow rate to the pre-established set point.

An increment supply of modifier is introduced through line 68 into line 130 and thereby enters the polymerizing mixture. The points of addition of such increment modifier may be at any point in the effluent of a reactor at least one third of the way down the series of reactors in the chain and may constitute more than one point of addition.

A location of the conversion measuring means may be in the effluent stream of a reactor at least one third of the way down the series of reactors, further conversion measuring means being in the effluent stream of the terminal reactor in the series of reactors. The conversion measuring means determines the concentration

of polymer in the fluid stream at the point of measurement. Suitable means include, for example, the Model 506 Analicon Density Gauge manufactured by Nuclear-Chicago Corporation, 333 East Howard Avenue, Des Plaines, Illinois, in which a beam of gamma radiation is transmitted across a cell within the pipe in which the fluid stream is flowing and the amount of original radiation detected on the opposite side of the cell is determined. The amount of radiation which is determined (i.e. the non-absorbed radiation) is inversely proportional to the density of the fluid stream in the cell, the density being directly proportional to the solids content of the fluid stream, i.e. the monomer to polymer conversion. It is preferred to maintain essentially constant the temperature of the fluid stream passing through the cell.

Signals are generated responsive to the temperatures recorded in temperature recorder controllers 108, 118, 128, 138, 158, 168, 178 and 188, such signals being transmitted to computing means 501. Computing means 501 may also transmit signals in order to establish new set points in said temperature recorder controllers. Signals are generated responsive to the monomer-to-polymer conversion as determined by conversion measuring means 142 and 192 and are transmitted to computing means 501. Additional inputs to computing means 501 may be entered manually, as the result of external measurements such as Mooney measurement data and laboratory determined solids content of the aqueous streams.

Figure 3 illustrates an automated viscometer that may be used in the process of the invention to provide rapid results on a vistex viscosity measurement of polymer molecular weight. Figure 3(a) illustrates how such a viscometer may be incorporated into the process layout. Line 300 is a pipe carrying the effluent from one of the reactors of the chain of reactors of Figure 2. A by-pass or loop line 302 carries a small proportion of the total stream flowing through line 300. In the by-pass line 302 is a Y-strainer 304 which serves to remove any particulate material which might inadvertently be in the line. The fluid stream passing through line 302 then passes through a sample valve 306, a back pressure valve 308 and thence by line 310 back into the main fluid stream in line 300. This arrangement permits the continual flow of the fluid in line 300 through the by-pass, thereby ensuring that any sample removed in sample valve 306 is fully representative of the fluid in line 300. The fluid flowing in line 300 is always maintained at a temperature different from the ambient temperature: a thermometer 312 is incorporated into line 310 and serves to demonstrate the presence of the fluid in the line. Figure 3(b) illustrates a cross-section taken through sample valve 306. The sample valve comprises an outer retainer 320 with a movable slide piece 324 having a circular aperture of accurately known volume defined by the aperture diameter and movable slide piece thickness. The by-pass line 302 is connected to the outer retainer and the movable slide piece, as shown, allows the flow of fluid through the valve. Line 322 is also connected to the outer retainer and connects the valve to a source of solvent for the polymer. When movable slide piece 324 is moved, by applying air pressure through valve 334 to line 336 and allowing air to vent through line 328 and valve 326, it isolates the fluid contained in the circular aperture therein and moves it into connection with line 322 whereby the fluid contents are flushed out through line 322 with the aid of the solvent supplied. Thus an accurately known and constant volume of the fluid is removed and transferred to the viscometer. The movable slide piece is then returned to the position shown in the figure by applying air pressure through valve 326 to line 328 and allowing air to vent through line 336 and valve 334.

Referring to Figure 3(c), the sample valve 306 is shown with the lines 302 and 322 connected thereto. Container 358 is a solvent storage vessel which is connected by line 354 and valve 356 to line 322. Also attached to line 322 is a pipette 350 of accurately known volume. Pipette 350 is filled by opening valve 356 when solvent from storage vessel 358 flows in, any excess overflowing back to the storage vessel by line 352. Subsequent operation of sample valve 306 isolates the fluid contained within movable slide piece 324, and thereby obtains a sample of accurately known volume, and puts the sample in connection with line 322 and the known volume of solvent in pipette 350 flushes the sample into mixing vessel 370, which contains an agitating means 372. The sample and solvent are retained in the mixing vessel, while being agitated, for a sufficient time to permit the polymer of the sample to be essentially totally dissolved in the solvent. Opening of valve 376 allows the polymer solution to flow through line 374 through a heat transfer coil 378 surrounded by water from the viscometer bath at a constant temperature. Opening of valve 380 allows the solution to flow through an in-line filter 386 into the bulb 390 of a capillary viscometer, said viscometer being suspended in a constant tem-

perature bath 392. The viscometer may be of any type suitable for measurement by flow through a capillary of a vistex viscosity of a polymer and is illustrated by an Ubbelohde viscometer. The viscometer is a combination of a length of capillary tube 400 maintained in an essentially vertical position having two bulbs attached thereto and a length of wide bore tubing 402, the capillary tube being the essential component for the measurement of said vistex viscosity. Built into the capillary tubing, being vertically spatially separated and located one above and one below the lowest of the bulbs attached to the capillary, are liquid level detectors 394 and 396 such that they act as references for the detection of the time when the polymer solution has just passed each of the two reference points and thereby defining a predetermined volume in the capillary tube. Said liquid level detectors are connected to an electronic timing device 471 capable of measuring time with an accuracy of 0.01 seconds, whereby a flow time may be measured from level detector 394 to level detector 396 for the flow of the polymer solution through the capillary of the viscometer, said flow of polymer solution being at constant pressure. In order that pure solvent may be brought into the viscometer, for cleaning purposes and for determination of the flow time of pure solvent through the capillary, line 381 connects the solvent storage vessel 358 with the entry to the viscometer through valve 383. Line 408 connects the capillary tube 400 to a source of vacuum through valve 414, to a source of air pressure through valve 412 and to a waste discharge line and atmospheric connection through valve 410. The wide bore tubing 402 of the viscometer is connected by line 404 and valve 406 to a waste discharge line and atmospheric connection. Line 382 into the viscometer is connected by valve 384 to a source of vacuum. Operation of valves, 356, 326, 334, 376, 380, 383, 384, 406, 410, 412 and 414 is controlled by a controller 451, such as a step-by-step relay or card program control unit, whereby each stage of the operation is sequentially controlled by operation of the valves in the necessary order. The start of such a sequence of operations or cycle would suitably be the removal of a sample of the fluid in line 302 by movement of movable slide piece 324 through the operation of valves 326 and 334 to vent and to air pressure respectively. The solvent in pipette 350 flushes the sample into mixing vessel 370 from which, after a suitable time of mixing of say five minutes, valve 376 opens to allow the polymer solution to pass through heat exchanger 378. With valves 383 and 384 closed, opening of valve 380 transfers the polymer solution into the viscometer 390 following which valve 380 is again closed. With valves 406, 412 and 410 closed, opening of valve 414 causes the polymer solution to rise up tube 402 and capillary 400, valve 414 being closed when the solution passes detector 394. Opening of valves 406 and 410 allows the solution in capillary 402 to flow down the capillary under atmospheric pressure, the flow time between the two level detectors being measured by timing device 471. This timing cycle is repeated at least once more and the polymer solution is then flushed out of the viscometer, by closing of valves 406, 410, 414, 380 and 383 and opening valve 412 allowing air pressure to force the solution out of open valve 384. Valves 412 and 384 are closed, valves 406 and 410 opened and pure solvent enters the viscometer through valve 383. The solvent is flushed out of the viscometer in the same manner as the polymer solution and the solvent flushing repeated a second time. Solvent is again allowed into the viscometer and the flow time measured, in duplicate, for the flow of pure solvent between the two level detectors. Removal of the solvent from the viscometer would complete the use cycle.

Signals representative of the vistex or solution flow times and the solvent flow times are generated by electronic timing device 471 and transmitted to computing means 501.

Suitable location of sampling valve 306 may be, in Figure 2, in line 140 and in line 190, wherein the conversion of monomers to polymer are accurately known and thereby the polymer concentration in the solution used for viscosity measurement would also be accurately known.

In order to describe mathematically the polymerization process, it is necessary to understand all the components which make up the process. Soap solutions form micelles, or particulate-behaving entities; when organic materials are present in the soap solution, some of the organic materials will diffuse into the micelles. The remaining organic materials will form droplets dispersed throughout the system. The organic materials referred to include the polymerizable monomers and chain transfer agent. Free radicals formed in the aqueous phase are captured in the micelles and initiate polymerization therein. The initial stages of the polymerization occur in the micelles and, at a stage determined by the amount of soap present, polymer particles separate out. These polymer particles also contain dissolved monomer, catalyst,

modifier and soap and, depending on the monomer types, may be swollen because of the solubility of the polymer in the monomer. Polymerization continues in these polymer particles which are supplied by diffusion of the molecules throughout the aqueous phase with additional monomers and transfer agent from the droplets dispersed throughout the system. The polymerization is thus zero order in monomer. When all the dispersed droplets have been used up, the polymerization reaction then becomes dependent on the concentration of the monomers present, and not replaced, in the polymer particles, thus becoming first order in monomer due to the fact that the only available monomer is that present in the polymer particles. Termination of polymerization is achieved by the addition of a shortstop, such as hydroquinone, which reacts rapidly with free radicals both from the initiator and the growing polymer chains.

The polymerization process encompassed by the scope of this invention may be exemplified by the polymerization of a monovinylidene compound and a diene. Examples of such monovinylidene compounds include styrene, alphamethyl styrene, acrylonitrile, methacrylonitrile, methyl acrylate and methyl methacrylate. The diene may be exemplified by butadiene and isoprene. A preferred embodiment of the process of this invention is the polymerization of butadiene and styrene. The butadiene-styrene polymerization process may be summarized by the following statements. The number of latex particles is essentially constant following the mixing together of the water, the hydrocarbon and the soap components thereby causing the formation of the initial latex particles, the number of latex particles depending, at a fixed monomer concentration, on, inter alia, the concentration of the soap in the aqueous phase and depending on the type of soap used. The number of latex particles depends on the number of free radicals or initiating species present, in other words, on the concentration of the initiator, because the interaction of the micelle concentration and the free radical concentration can be described by the initiator concentration at a fixed soap concentration. Each latex particle, once formed, polymerizes at a rate dependent only on the polymerization temperature (as it affects the propagation rate) up to about 50—60% conversion of the monomers. Hence the polymerization is a zero order reaction. At a later stage in the polymerization, above about 50—60% conversion, when all the free monomer droplets have been used up and no longer are available as sources of monomer, the reaction becomes first order in monomer because the only monomer available is that present in the swollen particles.

The mathematical representation of a continuous polymerization process is exemplified by the foregoing characteristics of butadiene-styrene polymerization. A first portion of the representation of the process reads on the conversion of monomers to polymer which is affected by the activator plus catalyst and a second portion of the representation reads on the molecular weight of the polymer formed which is affected by the rate at which the polymerization modifier is consumed.

In an operation of the process of this invention, as it applies to the free radical catalyzed emulsion polymerization of butadiene and styrene monomers, flow rates for butadiene, styrene, water, soap solution, initial modifier, activator, catalyst and increment modifier are set to pre-established rates. The temperature controllers for the feed cooling means and for each cooling means of each of the reactors are set to pre-established levels, the flow of refrigerant to the cooling means thereby being established. After the process has been running for a period of time, the flow rates shown by the process control instruments are transmitted to the computing means: thus the actual flow rates for butadiene, styrene, water, soap solution, initial modifier, activator, catalyst and increment as shown by flow recorder controllers 51, 52, 54, 55 and 56 and by metering pumps 33, 37 and 38, are transmitted, as signals representative of such flow rates, to the computing means. Details of the configurational layout of the chain of reactors, including reactor volume, point of addition of increment modifier (as from line 68) and location of conversion measuring means 142 and 192, are transmitted to the computing means. Signals are transmitted to the computing means representative of the temperature (temperature recorder controller 74) of the feed stream, of the feed cooling means and of the temperatures of the contents of each reactor (temperature recorder controllers 108, 118, 128, 138, 158, 178 and 188); set point temperatures are transmitted to the computer usually at the beginning of each run. The latest available results for a molecular weight of the rubber produced by the process, including at least one of a vistex viscosity as determined in solution and a Mooney viscosity as determined on a Mooney machine, are transmitted to the computing means, either as a calculated result or as a manual input: the rubber samples for such measurements are obtained at least from the

effluent of the terminal reactor of the chain (line 194 or sample point 196) and optionally from a sample line (line 144 or sample point 146) at a point within the series of reactors. Monomer to polymer conversion data, including results from the conversion measuring means 142 and 192 and optionally, externally determined polymeric solids determination, for at least the effluent of the terminal reactor of the series of reactors and optionally for the effluent of a reactor at least one third of the way down the series of reactors are transmitted to the computing means, either as signals representative of the conversion measured by the conversion measuring means or as manual inputs representative of externally determined results. Data on the purity of the butadiene and styrene feed streams, determined on a periodic basis by an external analytical means, are entered as manual inputs to the computing means.

Following the command so to do, the computer calculates a best estimate of the state of the process using certain of these inputs in pre-established kinetic equations. Using the total flow rate of all materials fed to the reactor chain and the volume of each reactor in the chain, the computer establishes a residence time for the polymerizing mixture in the chain and in each reactor in the chain. Using the measurements supplied to it for the temperature of the contents of each reactor and the now calculated residence time for the polymerizing mixture in each reactor, the computer calculates an expected reaction rate and establishes a calculated rate of disappearance, or consumption, for each of the chemicals in each reactor. Such calculations involve the use of four differential equations for each reactor in the chain, one equation being directed to establishing the conversion of monomers to polymer, one equation being directed to the rate of disappearance of activator and catalyst, one equation covering the rate of disappearance of modifier and one equation being directed to establishing a molecular weight for the polymer formed. The computer calculation also establishes what the steady state condition of the system would be if and when a steady state is achieved. The computer then compares its best estimate, as above, of the condition of the system with the presently inputted data on the actual present condition of the system such as the conversion of monomers to polymer and the molecular weight of the polymer. The comparison shows whether an upset in the system has occurred. Such an upset could be due to the presence of interfering impurities in the feed streams, due to the presence of an oxidant, for example oxygen, in the system or due to a mechanical problem in the system. The computer comparison will determine, if an upset has occurred, whether this upset is due to conversion related process variables or due to molecular weight related variables and the computer can then direct the necessary corrective action, as given below.

In order that the computer should not make incorrect recommendations for corrective action based on unrealistic or incorrect input data, the input data transmitted to it is first put through a computational cycle to assess the reliability of the input information. This computational cycle is an estimating filter which acts to compare the actual data transmitted to the computer with estimated minimum variance values calculated for such data and which could reasonably have resulted in the system. The computational cycle uses inputs on the actual past and present conditions of the system and corrective actions that have been put into effect in the system and calculates predicted values based on minimum variance, for the inputs to be transmitted to it. These calculated predicted values are then compared with the immediate next inputs transmitted to the computer. Where any actual particular inputs are at variance with the predicted values, the computer is programmed to place less reliance on its use of that actual input and to assume a more realistic value for that input.

In the actual control of the process, the computer is programmed to undertake a series of computations using past and present input data to adjust the parameters of a series of differential equations which will describe the present state of the system. These computations involve a series of integrations of the differential equations following a prescribed iterative algorithm to obtain new values for the parameters of the differential equations such that the differential equations do describe the present state of the system. The differential equations with the newly calculated parameters are then used by the computer as a best estimate of the present state of the process, which estimated present state is compared with a pre-determined desired state of the process. By such a comparison a difference is established between the best estimate of the present state of the process and a pre-determined desired state of the process. If this difference exceeds a predetermined level then the computer calculates new flow rates for at least one of activator,



catalyst and modifier in order to cause the production of polymer of predetermined qualities as represented by a predetermined desired state of the process.

The consumption of catalyst plus activator at any point in the process may be described by a variable  $\xi$  in the form of a differential equation

$$\frac{V_j \rho_j}{K_3} \cdot \frac{d \xi_j}{dt} = F (\xi_{j-1} - \xi_j) \quad (i) \quad 5$$

where

$$\xi_j = K_c (\text{catalyst}_j)^r (\text{activator}_j)^s \quad (ia) \quad 10$$

$V_j$  is the volume of the  $j$ th reactor,

$\rho_j$  is the density of the latex in the  $j$ th reactor,

$F$  is the total flow rate for monomers into the reactors,

$(\text{catalyst}_j)$  is the flow rate of catalyst into the  $j$ th reactor,

$(\text{activator}_j)$  is the flow rate of activator into the  $j$ th reactor,

$\xi_j$  describes the activator and catalyst in the  $j$ th reactor,

$K_3$ ,  $r$  and  $s$  are empirical constants, and

$K_c$  is a statistical parameter adjusted to fit the equation to describe the process and is discussed hereinbelow.

The conversion of monomers, for example styrene and butadiene, to polymer and the effect of catalyst and activator on the conversion is described and controlled to achieve the predetermined conversion by the equation

$$\frac{V_j \rho_j}{K_1} \cdot \frac{d X_j}{dt} = F (X_{j-1} - X_j) + \frac{V_j \rho_j}{K_2} \cdot (XR)_j \quad (ii) \quad 20$$

where the instantaneous reaction rate in the  $j$ th reactor  $(XR)_j$  is given by

$$(XR)_j = \xi_j e^{(-\Delta H/RT_j)} \quad (iia) \quad 25$$

when the reaction is zero order, e.g. when  $X < X_B$  and is given by

$$(XR)_j = \xi_j e^{(-\Delta H/RT_j)} \cdot \left( \frac{1 - X_j}{1 - X_B} \right) \quad (iib) \quad 30$$

when the reaction is first order in monomer, i.e. when  $X > X_B$ ; where

$X$  is the fractional conversion of monomers to polymer,

$X_j$  is the fractional conversion of monomers to polymer in the  $j$ th reactor,

$X_B$  is the fractional conversion where the reaction becomes first order in monomer,

$(XR)_j$  is the polymerization rate in the  $j$ th reactor,

$\Delta H$  is the activation energy of propagation,

$T_j$  is the temperature in the  $j$ th reactor, and

$K_1$  and  $K_2$  are empirical constants.

In equation (ii), the left hand side describes the rate of accumulation or loss of polymer due to a change in the conversion of monomer to polymer in the  $j$ th reactor.

The right hand side of the equation defines the net generation of polymer in the  $j$ th reactor with due allowance for flow of polymer into and out of the  $j$ th reactor. The

computer is programmed to utilise either the zeroth or the first order rate equation depending on a predetermined conversion limit  $(X_B)$ , the conversion in each reactor

in the chain being calculated and compared with  $X_B$  in order that the computer may select the rate equation to use for the conversion calculation in the next reactor. The

reaction rate terms of equation (ii) depend on the variable  $\xi_j$ , and in this way the computer assesses whether to raise, lower or leave unchanged the activator plus catalyst in

order to bring the process in line with the predetermined conversion aiming point by comparing the calculated conversion with the measured conversion. In an actual computational cycle, the computer is programmed to test that the model is a valid



representation of the process by an estimating computation, which is outlined herein-after.

Having a method whereby control of conversion of monomers to polymer may be achieved, it is then necessary to have a method for the control of the molecular weight of the polymer. The polymer molecular weight is controlled by chain transfer to the modifier, so that to describe the polymer molecular weight it is necessary to be able to define the modifier concentration at any point in the chain which is then used to calculate the polymer molecular weight. The net rate of consumption of modifier in the reactor chain is given by

$$\frac{V_j \rho_j}{K_6} \cdot \frac{d S_j}{dt} = F [S_{j-1} + (SF)_j - S_j] - \frac{V_j \rho_j}{K_7} \cdot K_8 S_j \quad (\text{iii})$$

where

$S_j$  is the concentration of modifier in the  $j$ th reactor,

$(SF)_j$  is modifier added (i.e. incremental modifier) to the  $j$ th reactor,

$K_6$  and  $K_7$  are empirical constants and,

$K_8$  is a constant defined by the chemical nature of the modifier.

The polymer molecular weight is affected by the modifier concentration which is given and controlled to achieve the predetermined molecular weight by the equation

$$\frac{v_j \rho_j}{K_4} \cdot \frac{d ([\eta]_j x_j)}{dt} = \frac{v_j \rho_j}{K_4} \cdot \left[ x_j \frac{d [\eta]_j}{dt} + [\eta]_j \frac{dx_j}{dt} \right] \\ = F(x_{j-1} [\eta]_{j-1} - x_j [\eta]_j) + \frac{v_j \rho_j}{K_5} (XR)_j K_v \cdot \left[ \frac{M_m (XR)_j}{K_8 S_j} \right]^\alpha \quad (\text{iv})$$

where

$[\eta]$  is the intrinsic viscosity, i.e. a vistex viscosity, of the polymer in the  $j$ th reactor,

$M_m$  is the molecular weight of the modifier,

$K_4$  and  $K_5$  are empirical constants,

$K_v$  is a parameter adjusted to fit the equation to the process and is discussed hereinbelow, and

$\alpha$  is the empirical Mark-Houwink constant.

The polymer Mooney is related to the intrinsic viscosity and conversion by the equation

$$\text{Mooney} = A + B \cdot \frac{X[\eta]}{X + C} \quad (\text{v})$$

where  $A$ ,  $B$  and  $C$  are empirically determined constants and the intrinsic viscosity is a specific form of a vistex viscosity. Equation (iv) is used in the computations to control the molecular weight of the polymer, the conversion already being known, by means of variation in the quantity of increment modifier added to the chain. For example, if the conversion is at an acceptable level but the product Mooney is too high, the necessary increase in modifier may be calculated to bring the product Mooney back to the desired point. In the event that both the conversion and Mooney are not at the desired aiming points, the computer can calculate the necessary changes in activator and catalyst to restore the conversion to the required level and the necessary change in increment modifier to bring the molecular weight to the desired level, the interaction due to the change in conversion being incorporated into the calculation of the change in increment modifier.

Because of the dynamic nature of the differential equations and the fact that they can be used to predict the state of the system at any time in the future, the effect of changes on product quality at a future time can be calculated. If, for example, the molecular weight is very far from the aiming point, a great excess of increment modifier can be added, for a short time, to the process in order to rapidly drive the molecular weight to the aiming point followed by a decrease in increment

modifier addition rate at a time calculated to be slightly before when the process is achieving the aiming point. By such means, in combination with calculations as the process responds to the change in increment modifier, it is possible to correct the process without overshooting the aiming point.

The parameters  $K_c$  and  $K_v$  are utilized to achieve a fit of the mathematical models to the actual plant process. This is done through a filter-estimating computational cycle. The filter-estimating cycle performs two functions. One such function is to screen the incoming data or inputs based on the data reliability or established standard deviations associated with each test result. The second function is to calculate, on the basis of assumed random disturbances in the process and assumed dynamic behavior of the process as defined by the process differential equations, a minimum variance estimate of the present state of the process. The computer utilizes (i) the previous best estimate of the state of the process and the parameters  $K_c$  and  $K_v$ , (ii) certain of the immediate past history of the process behaviour and (iii) any process changes, including changes in incremental modifier, catalyst and activator, that have been made to the process and by calculations involving the integration of the differential equations forming the process model determines an updated estimate of the state of the process. Newly obtained inputs of process measurements are compared with the updated estimate. This comparison includes allowance for previously established standard deviations for the process measurements. If a significant difference is found between the updated estimate and the newly obtained inputs, an iterative computational cycle is used by the computer to adjust the parameters  $K_c$  and  $K_v$  so as to rationalize the process model to the measured process state. By this means random process disturbances are accounted for and incorporated into the new model of the process and only after this has been achieved does the computer calculate if any process control action is needed.

Data from the process control equipment can be transmitted to the computing means at any desired frequency. Data from the conversion measuring means may also be transmitted to the computing means at any desired frequency. Additional data on conversion, obtained by laboratory determined polymer content of the latex at specific sampling points, may be manually entered into the computing means on a periodic basis. Vistex viscosity data, as from the automated viscometer, may be transmitted to the computing means at a rate determined by the time cycle for measurement in the viscometer. Mooney measurement data on product obtained at specific sampling points may be transmitted to the computing means at a frequency determined by the time necessary for sample preparation and Mooney measurement. The frequency at which Mooney data is transmitted to the computing means is usually rather low compared to the frequency at which the other data are available to the computing means. The advantage due to incorporating an automated viscometer for the determination of the vistex viscosity, with a short time cycle for sampling and measurement, and due to the rapid calculation of the state of the process, can clearly be seen in reference to maintaining the process at the predetermined aiming points for the majority of the operating time.

#### WHAT WE CLAIM IS:—

1. An improved continuous emulsion polymerization process for the production of a polymer having predetermined qualities comprising an average molecular weight and conversion of monomer to polymer, said process comprising:

(a) feeding at controlled flow rates a plurality of fluid feed streams to a first reactor of a plurality of reactors in series, each reactor being maintained at an essentially constant temperature, each of said fluid feed streams being a major source of one of at least one polymerizable monomer, soap solution, water, catalyst, activator and modifier;

(b) subjecting the reaction mixture formed by said fluid streams in said reactor to polymerization conditions; and

(c) measuring the density of a fluid comprising an aqueous latex of polymer of tentative of the flow rate of a respective one of said plurality of fluid feed streams or the terminal reactor of the series of reactors and, optionally, at a point at least one third of the way down the series of reactors, and recovering from the terminal reactor of said series of reactors a polymer having the predetermined qualities, the improvement comprising:

(i) determining within the process a vistex viscosity for polymer obtained from the effluent of at least the terminal reactor of the series of reactors;

(ii) generating a plurality of first signals, each of said first signals being repre-

sentative of the flow rate of a respective one of said plurality of fluid feed streams or of the temperature in a respective one of said reactors;

(iii) generating a plurality of second signals, each of said second signals being representative of said measurement of fluid density;

5 (iv) generating third signals, each third signal being representative of the measurement of a vistex viscosity; 5

(v) generating fourth signals, each fourth signal being representative of the Mooney viscosity of a dry sample of polymer of said polymerizable monomer, said dry sample being obtained by drying a sample of the effluent of at least the terminal reactor of said series of reactors; 10

(vi) causing transmission of said first, second, third and fourth signals to a computing means; 10

(vii) operating said computing means to undertake computational cycles comprising calculating predicted values, based on previous signals, of the polymer qualities comprising an average molecular weight and conversion of monomer to polymer, determining by means of said predicted values of qualities and present values represented by presently received signals a best estimate of the present state of the process including the conversion of monomer to polymer and average molecular weight through the series of reactors, determining the difference between said best estimate of the present state of the process and a predetermined desired state of the process, determining whether said difference exceeds a predetermined level, when said difference exceeds said predetermined level causing said computing means to calculate new flow rates for at least one of activator, catalyst and modifier to cause the production of polymer of predetermined qualities; 15 20

(viii) generating, and causing the transmission, to means for controlling the flow rates, of signals representative of said new flow rates, thereby establishing said new flow rates, and 25

(ix) repeating said steps (vii) and (viii) on a periodic basis.

2. The process of claim 1 wherein the polymer is a polymer of a monovinylidene compound and a diene. 30

3. The process of claim 2 wherein said monovinylidene compound is styrene and said diene is butadiene. 30

4. The process of claims 1, 2 or 3 wherein the modifier is fed to the plurality of reactors as at least two fluid streams, a first stream being fed to the initial reactor of the series and at least one increment stream being fed to the effluent of a reactor at least one third of the way down said series of reactors and said new flow rate for modifier is applicable to said increment stream. 35

5. The process of claim 2 wherein the determining of said vistex viscosity comprises:

(a) removing a predetermined volume of a uniform sample of aqueous latex from the effluent of a reactor; 40

(b) dissolving said sample in a predetermined volume of an organic solvent to form a vistex solution;

(c) transferring said vistex solution to an essentially vertical capillary tube, maintained at a constant temperature, said capillary tube having two vertically spatially separated liquid level detectors thereby defining a predetermined volume in said capillary tube; 45

(d) filling said capillary tube with said vistex solution and draining under constant pressure said solution from said capillary tube past said two level detectors while measuring and recording the flow time of said solution between said detectors; 50

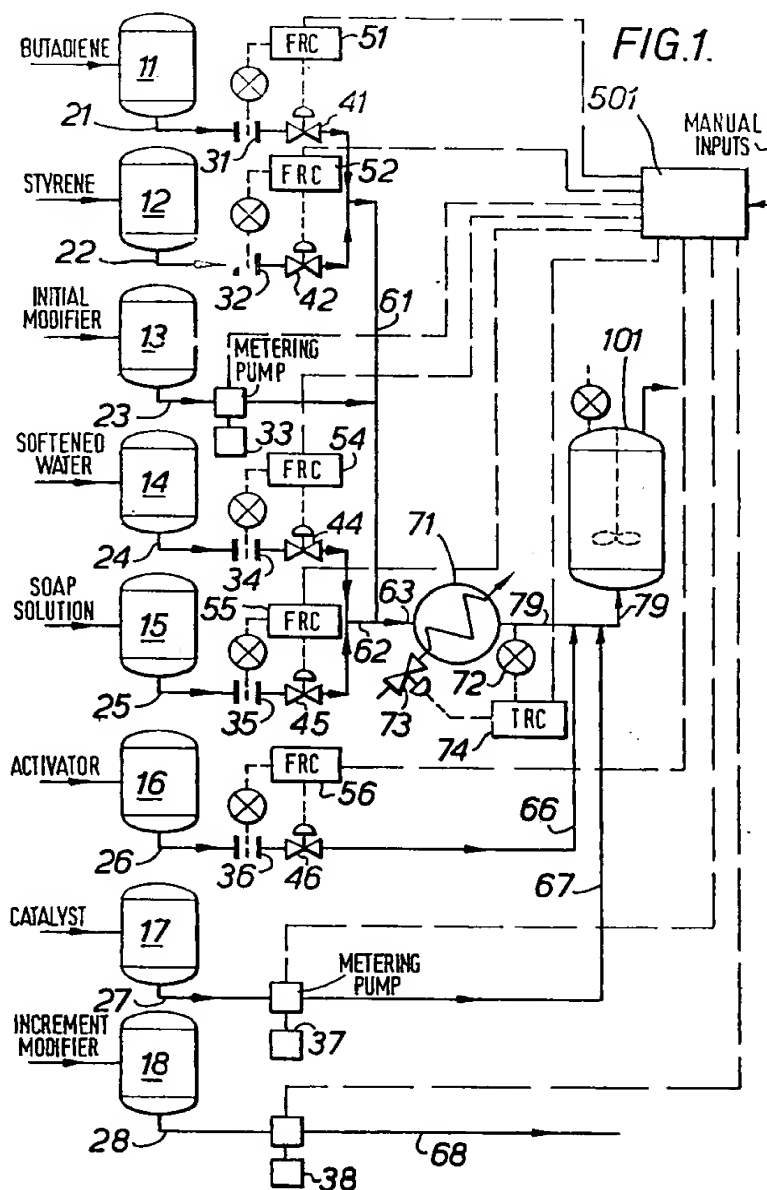
(e) filling said capillary tube with said organic solvent and draining under constant pressure said solvent past said two detectors while measuring and recording the flow time of said solvent between said detectors; and 50

(f) generating said third signals representative of said measured flow times for said vistex solution and said solvent, said steps (a) to (f) being repeatedly carried out in accordance with a predetermined program. 55

6. A process according to claim 1 substantially as hereinbefore described with reference to the accompanying drawings.
7. A polymer prepared by a process according to any preceding claim.

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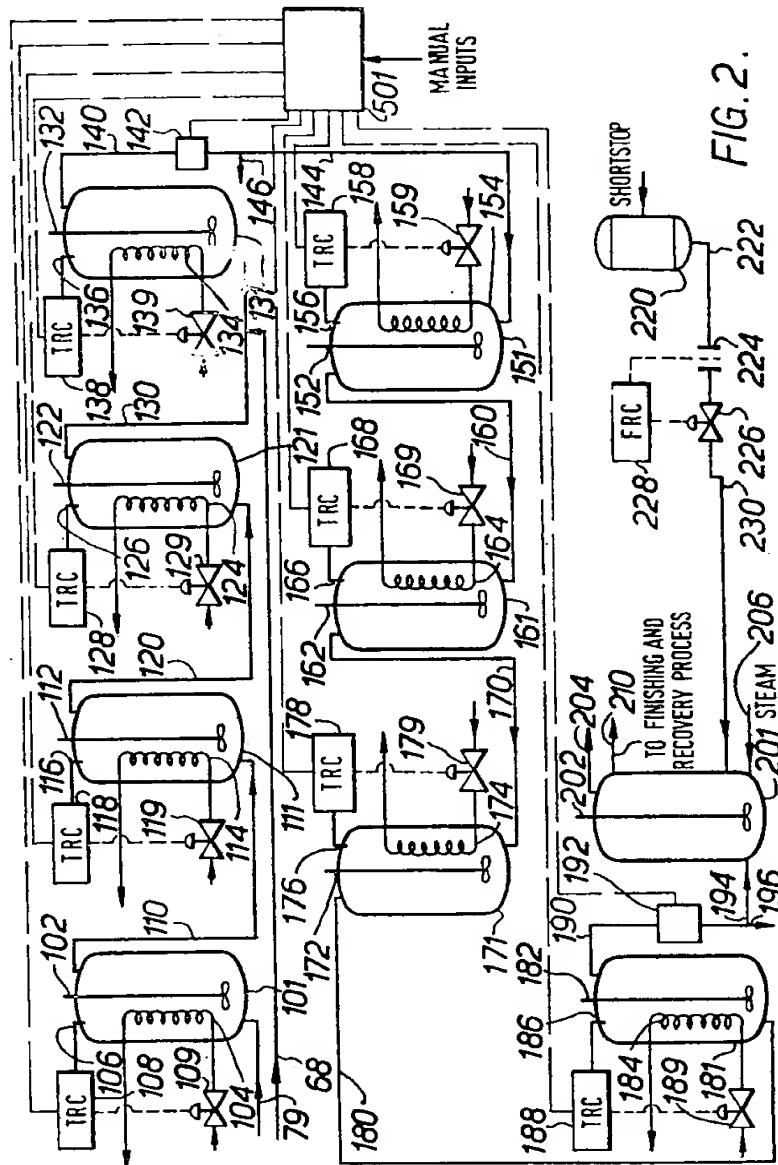


FIG. 2.

FIG. 3(a).

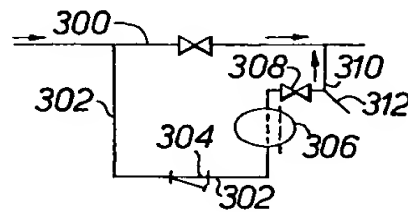


FIG. 3(b).

